



CERTIFICATE

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Presenter

International Conference on Concrete and Infrastructure (ICCI) 2015

*“Concrete Innovation and Application in Infrastructure
for Sustainable Development”*

Semarang, October 28-30, 2015

Dean of Faculty Engineering and
Chairman of ICCI 2015 Committee

Dr. Ir. Djoko Suwarno, MSI.



Prospect of Seawater Steel Structure Corrosion Study for Sustainable Development in Indonesia as the Tropical Country

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Abstract- Current and future development of coastal and ocean infrastructure for many goals such as for inter-ocean port, large scale shipyard and dockyard and also especially for coastal and ocean oil energy source development and exploitations has become a significant need. Thus has become a focus point around the world, which provides a huge marketing demand for the steel used in ocean engineering. Great potential study to develop steel with low cost and outstanding corrosion resistance to seawater. Many countries have developed sea-water corrosion-resisting steel, such as Mariner steel of America, Aps20A steel of France and Mariloy steel of Japan, which belongs to Ni-Cu-P series, Cr-Al series and Cu-Cr-Al series, respectively. Nowadays, people started to pay more attention to the effect of tin element on corrosion resistant property, especially after the successful development of high-tensile corrosion resistant steel containing tin in Japan in 2011. Many further study attempts to evaluate the effect of tin on corrosion resistant properties in sea-water corrosion-resisting low alloy steel. As well as increasing interest in using magnesium and its alloys because of their high strength to weight ratio, low density, high thermal conductivity, good ductility, high dimensional stability, maximum absorption of vibration, good electromagnetic, superior shielding and damping characteristics, high stiffness, good machinability, excellent cast ability and recycling ability.

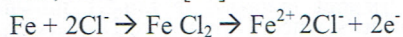
Keywords: steel-corrosion, seawater, tin, corrosion resistant steel

I. INTRODUCTION

Some seawater organisms and bacteria related to steel corrosion are *Anaerobik bacteria* (*Sulfate Reducing bacteria*), *Desulfobrio*, *Clostridia*, *Pseudomonas*, *Teredo.sp* and *Barnacle.sp*, *Aspergillus*, *Pinicillium*, *Torula*, *anemone* [1]-[2]. As revealed in some studies earlier that concrete steel in the seawater environments of 1.5 % (or 15ppt) will decrease its strength by 6.0 % [3]. Other than physical and chemical properties of the seawater, the seawater organism will also have tremendous impact to the corrosion of the concrete steel. In a research in Nathrang bay indicates that the more seawater organism grows on the surface of the carbon steel the more corrosion process in the carbon steel. This was especially *Sulfate Reducing bacteria* (SRB) will cause significant damage to the steel construction. The bacteria can survive in an aerobic condition and reducing of sulphate to become reactive acid solution that cause corrosion [4]. A comprehensive study at Jepara and Suramadu bridge at Madura were some good example of micro-organism and bio-fouling organism had revealed severe cause a structural damage of the concrete steel [5].

Corrosion is regarded as a decrease of steel quality and strength as impact of an electro-chemical reaction in seawater environment [6]. Corrosion as chemical phenomena on steel materials is an ionic reaction on the surface of the steel in seawater and oxydated environments. This was the main cause of the collapse of concrete steel structure such as bridges, overpass, jetty. Actually steel in a concrete structure will resist to corrosion since the alkaline properties of concrete protection on the surface of the steel in pH 12-13, until the breakdown of this concrete lamination on the steel in the concrete structures. The carbonation and intrusion of Chloride ions and CO₂ into the concrete structure will cause to the damage of the concrete steel structure. It was specifically mentions that atmospheric corrosion condition have more damage than a single factor condition [7]. The level of a coastal and in seawater steel

concrete corrosion will more severe than those in land condition [8]. In a study in Australia revealed that the level of corrosion in line with the level of salinity level of the area [9]. Studying on concrete steel with f_c is 30MPa, soaked in 3.5 % of NaCl had decrease the strength by 54.28 % [3]. Coastal erosion and sedimentation had also impacted on corrosion of port *causeway* [9]. As well as damage on the breakwater structure. In order to prevent corrosion is by aeration process into the seawater or by *Klorinasi*, *Tannates*, and *Potassium* [10],[2]. As active ion, Cl^- penetrates into the concrete structure and will react with the steel, as follows [11] :



More specific information that corrosion processes will increase in *splash zone*, this was since at this zone almost of all supporting element such as O_2 , Cl^- , H_2O , CO_2 were in abundance quantity. The corrosion rate on concrete steel structure will increase with high concentration of ion Cl^- and CO_2 , where *carbonation* process will occur and will cause that the concrete will more porous, lead to more seawater intrusion, more acid condition [11]. Furthermore, there are influence of external variables such as pH, oxygen, chloride, carbonation, water and humidity. Internal variables are cement type, aggregate-composition and quality of concrete.

II. SEAWATER MICROBIAL CORROSION

Sulphate reduces bacteria. The influence of sulfate-reducing bacteria (SRB) on the corrosion behavior of carbon steel was studied in a laboratory test-loop, continuously fed with nutrient supplemented North Sea seawater. The main parts of the test-loop, represented by two separated flow cells, were fitted with steel specimens. The test-loop was operating anoxically for 2200 h and each flow cell was three times inoculated with *Desulfovibrio alaskensis* or *Desulfovibrio desulfuricans* species. Additionally, each flow cell was two times perturbed with antimicrobial treatments. Steel specimens exposed in flow cells exhibited comparable appearance and systems responding similarly to inoculations and antimicrobial treatments. The effect of the inoculations in both flow cells on the steel electrochemical behavior was materialized as lower resistance to corrosion and higher surface activity or occurrence of localized pitting events. The localized surface attacks recognized in both flow cells after inoculations continued to progress with the time, although bacterial activity was temporarily suppressed by antimicrobial treatment. Post-exposure sample evaluations might suggest that, some particular steel surface areas have been subjected to a dramatic change in the corrosion mechanism from initial localized attack to general corrosion. The long-term exposure of the carbon steel specimens resulted in identifiable formation of biofilms and corrosion products. Corrosion deposits were characterized by a specific structure built of iron sulfides (FeS), sulfated green rust ($GR(SO_4^{2-})$), magnetite (Fe_3O_4), $Fe(III)$ oxyhydroxides ($FeOOH$), chukanovite ($Fe_2(OH)_2CO_3$), carbonated green rust ($GR(CO_3^{2-})$) and some calcareous deposits. Presented factual evidence reinforced the idea that sulfidogenic

species in natural seawater environment may cause localized damage with a specific surface pattern; however, this does not necessarily lead towards significantly elevated corrosion rates [12]. Internal corrosion causes immense damages to the carbon steel offshore infrastructures such as pipelines and injection systems. A significant part of the carbon steel degradation can be attributed to micro- and macro-environmental condition salteration by sulfidogenic, e.g. hydrogen sulfide (H_2S) producing microorganisms [13]. The most recognized group of sulfidogenic microorganisms are sulfate-reducing bacteria (SRB) and they are regarded as the main culprits of anaerobic corrosion in seawater system.

Within the marine biofilm matrix, SRBs thrive finding favorable conditions inside pre-established anoxic niches. In general, SRB including *Desulfovibrio desulfuricans* ATCC 27774 and *Desulfovibrio alaskensis* AL1, are performing dissimilatory reduction of sulfur compounds such as sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), polythionate (SnO_6^{2-}) and sulfur (S) itself to sulfide (S^{2-}), that, combined with oxidized molecular hydrogen, forms volatile H_2S negatively impairing ferrous metals [14]-[15]. Anaerobic corrosion is a well-understood process, exclusively controlled by the oxidizing agent/proton transfer to metal surface. However, in biotic environments different explanations were suggested in order to explain anaerobic corrosion process that resulted in elevated corrosion rates. During past few decades multiple theories explaining corrosion mechanisms were suggested by taking into account SRBs metabolic activities and formation of different sulfide based compounds. Even though SRBs are recognized as the most imminent species taking part in microbiologically influenced corrosion (MIC), microbial consortiums in marine biofilms are usually heterogeneous and therefore deterioration of metal should be affected by interactions of the whole community [16]. Some of the microorganisms commonly found in marine environments, such as acid producing bacteria (APB).

By reducing sulfate in sulfide, SRB promotes the conditions for precipitation of iron sulfide (biomineralized FeS , particularly FeS), which next catalyzes proton/water reduction into molecular hydrogen and acts as a cathode in a galvanic couple with metallic iron [17]-[20]. Direct products of SRB metabolism such as H_2S can affect metal surface directly by decreasing pH locally and promoting differential cell resulting with localized events on metal surface [21]. Metal ion chelating by extracellular polymeric substances (EPS) is also some-times dealt with [22] as well as galvanic coupling resulting EPS selective metal binding capacity [23]. To sum-up such a complex marine biofilm/corrosion products/metal interface, overlapping of proposed mechanisms should be considered rather than one specific mechanism [24]. It is often observed that the micro-environment generated within marine biofilms rich in SRB is favoring electrochemical reactions that may lead to localized destructive surface events [25]. Nevertheless, besides detrimental impact on steel integrity, the biomineralization process occurring on steel surfaces can be under favorable circumstances beneficial thought the

formation of protective corrosion products. The depth of the corrosion attack varies between approximately 20 μm to 40 μm on the specimen from the flow cell inoculated with *D. alaskensis*. The degree of damage is lower regarding depth, in range of approximately 20 μm , on the specimen from the flow in another cell indicating lower material deterioration.

III. METALIC COATING: TIN COATING

TiN (Titanium nitride) and TiAlN (titanium aluminium nitride) coating layers were fabricated on SKD 11 steel substrate by an arc ion plating (AIP) technique. The mechanical properties such as hardness, impact, and wear were comparatively examined between TiN and TiAlN coating layers. Those layers were fairly adherent to SKD 11 steel substrate, and showed hardness values of 2300 – 100 and 3200 – 100 kg/mm² with a load of 25 g, respectively. TiAlN coating layer showed much superior impact wear resistance to TiN layer. It could be suggested in this work that the TiN coating layer was failed relatively by plastic deformation with oxidation during impact test, while TiAlN coatings was failed by brittle fracture and resisted the oxidation by impact energy. However, TiN coating layer showed better the abrasive wear resistance than TiAlN. The friction coefficient of TiAlN films was higher than that of TiN films and considerably increased with increase of relative humidity due to the tribochemical reaction [26].

A new advanced sintered composite cutting tool has been developed based on tungsten carbide matrix ligated with cobalt (WC-Co) additivated with tantalum carbide (TaC), titanium carbide (TiC) and niobium carbide (NbC) as grain growth inhibitors. TiN, titanium carbonitride (TiCN) and TiAlN coatings were deposited on these tools by CAE-PVD (physical vapor deposition) technique to find out the best solution to improve the corrosion resistance of this tool in marine environment. The electro-chemical behaviours of the specimens in 3.5% NaCl water solution were estimated by potentiodynamic polarization measurements i.e. the open circuit potential (E_{oc}), corrosion potential (E_{corr}) and corrosion current density (i_{corr}). Wide angle X-ray diffraction (WAXD), optical microscopy (OM) and atomic force microscopy (AFM) investigations have been carried on tested and untested specimens to substantiate the corrosion resistance of the tested specimens. Based on the open circuit potential (E_{oc}) and corrosion potential (E_{corr}) results, the tested specimens were ranked as TiN, TiAlN, TiCN and WC-Co while on corrosion current density (i_{corr}) and protective efficiency (P) values they have been ranked as TiN, TiAlN, WC-Co and TiCN. The WAXD, MO and AFM results unambiguously show that the corrosion resistance depends on the nature and morphology of the coating [27].

Microorganisms tend to colonize on solid metal/ alloy surface in natural environment leading to loss of utility. microbiologically influenced corrosion or biocorrosion usually increases the corrosion rate of steel articles due to the presence of bacteria that accelerates the anodic and/or cathodic corrosion reaction rate without any significant

change in the corrosion mechanism. An attempt was made in the present study to protect hot-dip galvanized steel from such attack of biocorrosion by means of chemically modifying the zinc coating. W-TiO₂ composite was synthesized and incorporated into the zinc bath during the hot-dipping process. The surface morphology and elemental composition of the hot-dip galvanized coupons were analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy. The antifouling characteristics of the coatings were analyzed in three different solutions including distilled water, seawater, and seawater containing biofilm scrapings under immersed conditions. Apart from electrochemical studies, the biocidal effect of the composite was evaluated by analyzing the extent of bacterial growth due to the presence and absence of the composite based on the analysis of total extracellular polymeric substance and total biomass using microtiter plate assay. The biofilm-forming bacteria formed on the surface of the coatings was cultured on Zobell Marine Agar plates and studied. The composite was found to be effective in controlling the growth of bacteria and formation of biofilm thereafter [28].

IV. STEEL FATIGUENESS AND STEEL CORROSION

The mooring chains of off-shore petroleum platforms are designed for 30 years and loaded in fatigue in corrosive environment due to sea water. Because of the ocean waves (frequency varying between 0.1 and 1 Hz) for 24 hour a day, the number of load cycles during 30 years is between 9.5 to 107 and 9.5 to 108 cycles that is in the giga cycle regime (more than 108 cycles). This paper is focused on the effect of sea water corrosion on the giga cycle fatigue strength of a martensitic-bainitic hot rolled steel R5 used for manufacturing off-shore mooring chains for petroleum platforms in the North Sea. Some other studies have shown that defects like non-metallic inclusions, pores or pits are the key factors that control the fatigue behavior of metals in very high cycle fatigue (VHCF) regime. On the other hand, some studies have been proving that crack initiation dominates the total fatigue life of iron alloys in giga cycle fatigue in air [29].

V. DEEP SEA STEEL CORROSION

An evaluation of the current condition of sea-disposed military munitions observed during the 2009 Hawaii Undersea Military Munitions Assessment Project investigation is presented. The 69 km² study area is located south of Pearl Harbor, Oahu, Hawaii, and is positioned within a former deep-sea disposal area designated as Hawaii-05 or HI-05 by the United States Department of Defense. HI-05 is known to contain both conventional and chemical munitions that were sea disposed between 1920 and 1951. Digital images and video reconnaissance logs collected during six remotely operated vehicle and 16 human-occupied vehicle surveys were used to classify the integrity and state of corrosion

of the 1842 discarded military munitions (DMM) objects encountered. Of these, 5% (or 90 individual DMM objects) were found to exhibit a mild moderate degree of corrosion. The majority (66% or 1222 DMM objects) were observed to be significantly corroded, but visually intact on the seafloor. The remaining 29% of DMM encountered were found to be severely corroded and breached, with their contents exposed. Chemical munitions were not identified during the 2009 investigation. In general, identified munitions known to have been constructed with thicker casings were better preserved. Unusual corrosion features were also observed, including what are termed here as 'corrosion skirts' that resembled the flow and cementation of corrosion products at and away from the base of many munitions, and 'corrosion pedestal' features resembling a combination of cemented corrosion products and seafloor sediments that were observed to be supporting munitions above the surface of the seafloor. The origin of these corrosion features could not be determined due to the lack of physical samples collected. However, a microbial-mediated formation hypothesis is presented, based on visual analysis, which can serve as a testable model for future field programs [30].

VI. REFERENCES

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